Transitions in Ammonium Chloride-Ammonium Bromide Solid Solutions

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The temperatures at which ammonium chloride, ammonium bromide, and their solid solutions undergo the simple cubic $\rightleftarrows$ face-centered cubic transition have been investigated by various thermal methods. For both changes the observed temperatures pass through a minimum with change in composition. The position of the equilibrium solidus lines is estimated

THE HIGH TEMPERATURE (I) forms of ammonium chloride and ammonium bromide have a face-centered cubic lattice; the low temperature (II) forms have an interpenetrating simple cubic lattice. The I forms give a complete series of solid solutions (*6*), and so do the II forms (*2*). One would expect, therefore, that the transition temperature for the I $\rightleftarrows$ II change for the solid solutions would vary smoothly with their composition, with two solidus curves, delimiting the two-phase region, being required to represent the equilibrium relations. Even when moistened with solvent, however, the ammonium chloride–ammonium bromide solid solutions, when heated through the transition and sometimes when cooled through it, were found to transform reproducibly at a single temperature and not over a range. Varying the solvent contration between 12 and 20% makes no appreciable difference. X-ray patterns of the solids before and after such runs are identical. Each solution, moistened with solvent appears to behave as a pure substance, presumably because diffusion within the solid is effectively absent.

EXPERIMENTAL

Studies with the pure components were made using reagent grade salts recrystallized once from water and dried at 110° C. for at least 24 hours. The solutions were made from these materials by adding appropriate amounts of both to water, heating until they had dissolved, and allowing the solid solutions to precipitate by cooling to room temperature while stirring. The resulting suspensions were stirred for 3 to 12 weeks to effect homogenization, and then filtered, ground, and dried at 110° C. They were analyzed by dissolving in $1.5N$ H_2SO_4, oxidizing the bromide with excess 5% $KMnO_4$ solution, and permitting the free bromine to be dissipated by standing for a day or two. The excess permanganate was then destroyed with 3% H_2O_3 and the solution titrated potentiometrically with $0.1N$ $AgNO_3$. This procedure was found to be satisfactory by analysis of samples of known composition. The method avoids both boiling the solution to remove bromine, as described by Kolthoff and Stenger (*3*), and using acetone for the same purpose, as directed by McAlpine (*4*).

In the initial work the "static" method of thermal analysis, which Wood and his co-workers (*7*) had used for cesium chloride, was applied to the II → I change. For this, a sample of solid solution was held at a constant temperature for 30 minutes and then rapidly cooled or heated, the temperature being measured as a function of time. Thus a series of lower temperatures at which a change from II to I could be detected within 30 minutes, and a series of higher temperatures, at which the presence of unchanged II could no longer be detected after 30 minutes, were obtained. While, for a given sample, these temperatures could be reproduced to within a few tenths of a degree, a fresh sample from the same original batch gave results differing by as much as 5°, and the method was discarded in favor of a dynamic method.

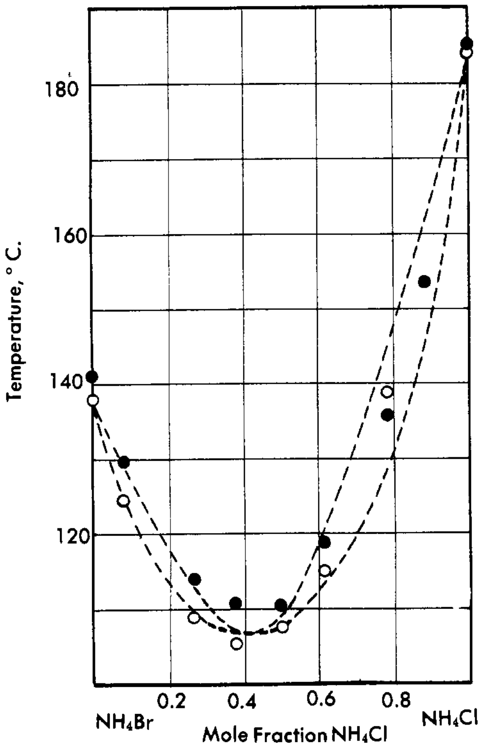

Figure 2. I $\rightleftarrows$ II transition temperatures of ammonium chloride-ammonium bromide solid solutions

● Differential heating
○ Differential cooling
----Estimated equilibrium solidus lines

Transition temperatures reproducible to 2° and frequently to less than 1° were obtained by using 7 grams of each solid, ground to 200-mesh and mixed with about one-fifth its weight of Baker Analyzed glycerol, heated by an oil bath. Temperatures were measured with a calibrated iron-constantan thermocouple. Rates of temperature change averaged about 0.25° per minute. Each run was preceded by a quick heating through the transition and quick cooling back again, for the purpose of "seasoning," as practised by Bridgman (*1*).

RESULTS AND DISCUSSION

The static method (data not presented) gave results qualitatively in agreement with those obtained by thermal analysis, and, in particular, showed that the temperature coefficient of the II → I reaction rate is greatest near a mole fraction of 0.5.

Differential thermal analysis gave the following results (mole fraction of ammonium chloride, ,transition temperature on heating (°C.), transition temperature on cooling (°C.): 0, 141.2, 138.1; 0.083, 129.7, 124.7; 0.269, 114.0, 108.9; 0.378, 110.8, 105.4; 0.498, 110.6, 107.7; 0.615, 118.9, 115.1; 0.785, 135.8, 138.7; 0.885, 153.5, unobservable; 1.000, 185.0, 184.1. These data are shown in Figure 1. Bridgman, (*1*) gives 137.8 and 184.3° and Pöyhönen (*5*), in a recent careful study, 137.2 and 183.1° for the pure bromide and pure chloride, respectively.

For the solid solutions, the observed temperatures of transition vary smoothly and pass through a minimum with changing composition. The II → I transitions occur at higher temperatures than the I → II, except for the solutions of highest chloride content where a large spread between the two equilibrium solidus lines is indicated (estimated, in the light of this investigation, as lying approximately as shown in Figure 1 by broken lines). This spread was further suggested by less noticeable thermal effects in this region.

ACKNOWLEDGMENT

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Interfacial Tension in Multicomponent Aqueous - Organic Systems

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Interfacial tension measurements are presented for four two-phase liquid systems: benzene–carbon tetrachloride–water, benzene–carbon tetrachloride–water–methanol, benzene–carbon tetrachloride–water–acetone, and benzene–carbon tetrachloride–water–cyclohexanol. Data are given both for freshly formed interfaces with the solute (4th component) originally in the organic phase, and for equilibrium phase compositions. The range of solute concentrations studied was from 0 to 50 mole %. Variations in interfacial tension as an effect of the solute ranged from 0 to 35 dynes per centimeter. Methanol decreased interfacial tension almost in proportion to concentration. Acetone had a proportionately greater effect at lower concentrations. The low concentration effect was even more pronounced with cyclohexanol.

ALTHOUGH INTERFACIAL TENSION data on many two-component, liquid-liquid systems are available in the literature (*1*), there is scant information on three or four component systems. Correspondingly, there are few, if any data on the effect of a solute, in either phase or in both phases, on interfacial tension in liquid-liquid systems.

This work presents interfacial tension data on the following multicomponent systems:

1. Water-Benzene-Carbon Tetrachloride
2. Water-Benzene-Carbon Tetrachloride-Methanol
3. Water-Benzene-Carbon Tetrachloride-Acetone
4. Water-Benzene-Carbon Tetrachloride-Cyclohexanol

In the last three systems, the final component was added initially to the organic phase. Thus freshly formed interfaces of nonequilibrium concentration distribution could be examined. The same systems were also studied with equilibrium distribution of concentration between the phases to provide interfacial tension data that was not time dependent.

APPARATUS

Interfacial tension data were obtained by use of a DuNouy interfacial tensiometer, catalog No. 93010 from Scientific Technical Supplies Co. of Frankfurt, Germany. The ring used was a No. 70542 platinum ring supplied by the Central Scientific Co. The mean circumference of the ring was 5.991 cm. The ratio of ring diameter to wire diameter, R/r, was 53.6. All experiments were conducted at ambient temperature.

Ternary phase diagrams for the systems studied were determined by titration where literature data were not available. Tie lines for the Benzene–methanol–water system were determined experimentally. Tie-line information for the other systems was obtained from Perry (*2*) and Seidell (*3*).

MATERIALS

All chemicals used in these experiments were Merck reagent grade, conforming to ACS specifications, with the exception of cyclohexanol. The latter chemical was provided by the Eastman Organic Chemicals Co.

EXPERIMENTAL

Interfacial tension data reported here are based on freshly formed interfaces with nonequilibrium concentration distribution and on equilibrium concentrations in each phase.

To obtain information on freshly formed interfaces, the following procedure was used: Phase 1, the organic phase, was made up to a known concentration by volumetric